XVII. "On the Spectrum of Nitrogen." By ARTHUR SCHUSTER, Student at the Physical Laboratory of Owens College. Communicated by BALFOUR STEWART, F.R.S. Received June 13, 1872.

1. *Introductory.*—The formation of the different spectra which one gas is said to exhibit, when examined under different conditions, still remains one of the most obscure points of spectrum analysis. In 1864, when Plücker and Hittorf published their researches "On the Spectra of Ignited Gases and Vapours, with especial regard to the different Spectra of the same elementary gaseous substance"*, they drew attention to the close resemblance in character of the band-spectra which certain metals yield at a comparatively low temperature to the band-spectrum of nitrogen and sulphur. Roscoe and Clifton, n their paper "On the effect of increased Temperature upon the nature of the Light emitted by the Vapour of certain Metals or Metallic Compounds" †, rendered it probable that the band-spectra of the metals belonged really to the oxides. The two spectra of nitrogen were not, however, examined from that point of view, but, on the contrary, they were made the starting-point of new investigations by Wüllner, who came to the conclusion that certain gases may give even more than two different spectra. Ångström ‡, expressing his doubts about the trustworthiness of Wüllner's experiments, says in a note: "As regards the spectra which are usually attributed to nitrogen, I mention here, as a general fact, that it is my conviction that the fluted bands which are so characteristic of the oxides of metals are never found in spectra of elementary gases."

I propose to show, in the present communication, (1) that pure nitrogen gives only one spectrum; (2) that this is the line-spectrum; (3) that the fluted spectrum of the first order is due to oxides of nitrogen, formed under the influence of the electric spark.

2. *First experiment.*—The first experiment which I made with respect to the spectrum of nitrogen, was a repetition of an experiment of Secchi, who found that in different sections of the same tube three different spectra of nitrogen might be obtained. A vacuum-tube was made exactly according to Secchi's description, filled with nitrogen and exhausted. To my astonishmemt the tube showed, even in its widest parts, only a spectrum of lines. No accurate measurements were taken at the time, but the spectrum was no doubt that of the second order described by Plücker. Suddenly, and while I was looking through the spectroscope, the spectrum changed, and the well-known fluted bands appeared. The first spectrum could now easily be obtained by introducing a Leyden jar in the circuit. The spark very soon ceased to pass, and it was then found that the tube was leaking.

3. The behaviour of this tube at once suggested the idea that the presence of air was necessary for the formation of the fluted spectrum. It is

* Philosophical Transactions, vol. clv. p. 1.
† Chemical News, vol. v. p. 233.
‡ Comptes Rendus, Aug. 1871.

well known that the oxides of nitrogen are formed on passing the electric spark through air, and the resemblance which this spectrum bears to the spectra of the oxides of metals rendered this view probable. In order to test it, a series of experiments were made, showing that,—

(*a*) Whenever the fluted spectrum appeared, it could be shown that traces of oxygen were present;

(*b*) Whenever there was a certainty of no oxygen being present, the spectrum of the second order appeared under all pressures and in all temperatures.

In order to free the nitrogen from every trace of oxygen, I adopted, at Dr. Stewart's suggestion, the plan of heating a small piece of sodium placed in the vacuum-tube. This proved in each case perfectly satisfactory; for when every trace of oxygen had thus been absorbed, the line-spectrum alone was invariably obtained*.

4. *Wave-length of the two spectra.*—There is no possibility of confounding the two spectra. The fluted spectrum is well known by its beautifully shaded violet bands; but in order to exclude any possibility of error, their position was read off on the reflecting scale of the spectroscope; the measurements were reduced to wave-lengths, and the following numbers obtained for the least refrangible end of the bands in tenth metres†:—

Fluted Spectrum.	
5129	4436
4981	4390
4649	4318
4556	4237

As the measurements were taken merely for the sake of reference, they do not lay claim to great accuracy.

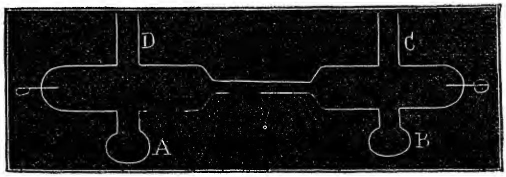
The true spectrum of nitrogen is easily recognized by a very bright green line followed at a small distance towards the more refrangible parts by a green band; it also contains some violet bands, which are not shaded. The position of the principal lines was read off; their wave-lengths, as determined by Dr. Marshall Watts from the measurements made by Plücker, are as follows:—

Line-spectrum.				
6243	5767		4214	band
6176	5666		4199	
6087	5164	(the green line)	4184	band
6051	4894		4170	
5908	4644			

* The formation of the fluted spectrum does not imply that all the nitrogen in the tube has been oxidized; it has been remarked by different observers, and especially noticed by Plücker, that when the spark passes through a mixture of two gases, the spectrum of one only is often seen.

† A tenth metre, according to Ångström, means a metre divided by 10^{10}.

5. *Description of apparatus.*—The tubes generally used had two pockets, A and B, into which small pieces of metallic sodium were introduced by means of the tubes C and D. The tube C was connected with the receiver



containing the nitrogen, whilst the tube D was connected with the air-pump. The nitrogen was generally prepared by the combustion of phosphorus in air. After a few hours' standing, when all the phosphoric acid formed had been absorbed, the gas became quite clear and was ready for use. This mode of preparation, it is true, does not give the nitrogen very pure; but as my object was to get the nitrogen free from oxygen, and this was easily obtained by means of the absorption by sodium, the method was found sufficient. Other modes of preparing the nitrogen were tried, such as passing air over red-hot copper or the decomposition of ammonia by chlorine, but the same results were invariably obtained. The air-pump used was that of Carré's freezing-machine, with which pressures down to 2 millims. could be easily obtained. When the pressure was measured, a T-shaped tube was employed, one side of which was connected with the Geissler's tube, the other with the pump, while the mercury was drawn up in the longer part of the tube; its height was read off and compared with a barometer. I now pass to the description of the experiments.

6. *Method of experimenting.*—When the air in the vacuum-tube had been exhausted, the communication with the receiver containing the nitrogen was opened, and the gas was allowed to pass through it for some time while the pump was being worked. The tubing connecting the tube with the receiver was then clamped air-tight, and the tube was exhausted.

The electric spark in passing through it exhibited a violet colour, and gave the spectrum of fluted bands:

5129	4436
4981	4390
4649	4318
4556	4237

The sodium was next heated until it presented a clean metallic surface. The light which the tube now emitted was bluish white, and much fainter than before; and the whole appearance of the spectrum had changed to that of the second order with its characteristic green line. It was, however, found that the pressure in the tube had slightly increased, owing most likely to the vapour of the sodium present; and on bringing the mercury to its former level, the spectrum became brighter, but remained the same in character. New nitrogen was then led into the tube, and after exhaustion the old fluted spectrum again appeared; this was, however, at once changed into that of lines by heating the sodium. This process was

repeated several times in succession, but invariably with the same result. I have in my possession two tubes sealed off under 2 millims. pressure, one without sodium, showing the fluted bands, the other containing sodium, showing the spectrum of lines. Two other tubes, sealed off under 15 millims. pressure, show the same thing. I have repeatedly convinced myself that, from the highest pressure under which the spark of the induction-coil passes to the lowest pressure which I could obtain with an ordinary air-pump, pure nitrogen invariably gave one and the same line-spectrum. Once, when I intended to seal a tube off under higher pressures, it was found that the sodium was not sufficient to absorb all the oxygen present, so that a sort of mixture of the two spectra was seen. Such a mixture was often observed by Plücker and Wüllner at the point where one spectrum changed into the other; it is characterized by the green line of nitrogen and the fluted violet bands at the same time.

The tube showing the mixture at 15 millims. pressure was gradually exhausted, but the spectrum remained exactly the same. If the formation of the two spectra depends merely upon the pressure or temperature to which the gas is subjected, how can a mixture of the two spectra, indicating a state of transition, exist under so entirely different pressures and different temperature?

In order to ascertain whether nitrogen even carefully prepared contains oxygen, a drop of a solution of iodide of potassium and starch was introduced into the tube; after the spark had passed for a few seconds only, the liquid was coloured blue—showing either the formation of oxides of nitrogen or of ozone, but at any rate the presence of oxygen.

7. *Spectrum of oxides of nitrogen.*—I tried to obtain the spectra of the different oxides of nitrogen; they all give the same fluted spectrum, and I could get no information as to which particular oxide the fluted spectrum is due: this is, however, easily understood if we remember that it is just as difficult to prepare the oxides of nitrogen free from oxygen as pure nitrogen itself; so that the oxide giving the spectrum in question will always be formed. I have, however, convinced myself that the absorption-bands of nitrous acid gas are not coincident with the bright bands of the spectrum; and it is probable that the spectrum is due to nitric oxide, this being the most stable of all the oxides of nitrogen.

I may add that one of the tubes containing the sodium and showing the lines one day cracked, and then at once showed the violet bands. This fact will not be easily explained by the assumption that the fluted spectrum belongs to a lower pressure and lower temperature than the spectrum of lines.

I propose to subject the different spectra of the remaining gases to a careful examination.

The above experiments were made in the Physical Laboratory of Owens College, Manchester; and I have to thank Professors Balfour Stewart and Roscoe for many valuable suggestions.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